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Peculiarities of the thermal donor formation in Czochralski grown silicon under high hydrostatic pressure

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ABSTRACT

Oxygen agglomeration processes leading to the formation of thermal donors in Czochralski grown silicon subjected to heat treatment at $T=450^{\circ}\text{C}$ at atmospheric pressure and a high hydrostatic pressure of $P=1$ GPa are studied. The samples investigated were doped with isoelectronic impurities of carbon and germanium. Both impurities are known to suppress the formation processes of thermal donors under normal conditions of heat treatment. It has been shown that the stress applied during heat treatment to Cz-Si with high concentrations of these impurities results in an enhanced formation of thermal donors. This effect is thought to be associated with increasing oxygen diffusivity under stress.

Keywords: silicon, isoelectronic impurity, hydrostatic pressure, oxygen aggregates, thermal donors.

1. INTRODUCTION

Czochralski grown silicon crystals (Cz-Si) contain high concentrations of oxygen, usually from $7\cdot 10^{17}\text{ cm}^{-3}$ to $9\cdot 10^{17}\text{ cm}^{-3}$. Because of a low solubility of oxygen in silicon below $T < 1000^{\circ}\text{C}$ oxygen impurity atoms form aggregates of different size upon annealing of silicon crystals at $T \geq 350^{\circ}\text{C}$. At relatively low temperatures of heat treatment at $T < 500^{\circ}\text{C}$ these agglomeration processes result in the appearance of Thermal Double Donors (TDD). This family of oxygen-related thermal donors consists of more than 16 centers whose shallow and deep energy states are in the ranges of $E_C - (40 \text{ to } 70)\text{ meV}$ and $E_C - (100 \text{ to } 160)\text{ meV}$, respectively. ¹⁻³ The donor centers mentioned are formed predominantly at $T < 500^{\circ}\text{C}$. Their maximal concentration in Cz-Si can be reached if heat treatment is performed at $T \approx 450^{\circ}\text{C}$.

Such isoelectronic impurities as carbon and germanium if present in high concentrations can strongly suppress the TDD formation. ^{1, 4-6} Pronounced effects of suppression are observed at impurity concentrations of $\geq 1\cdot 10^{17}\text{ cm}^{-3}$ and $\geq 1\cdot 10^{19}\text{ cm}^{-3}$ for carbon and germanium, respectively.

The aim of the present work is to shed new light on how the formation processes of thermal donors in Cz-Si:C and Cz-Si:Ge can be changed during heat treatment under high hydrostatic pressure. One could expect to observe some effects in view of strongly enhanced formation of oxygen-related thermal donors in normal Cz-Si subjected to annealing under stress. ^{7, 8}

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2. EXPERIMENTAL

Two wafers of Cz-Si doped with carbon and germanium were used. The initial materials were n-type. The concentrations of phosphorus were about $1 \cdot 10^{14} \text{ cm}^{-3}$ and $7 \cdot 10^{14} \text{ cm}^{-3}$ in the Cz-Si:C and Cz-Si:Ge, respectively.

The initial concentrations of oxygen in both wafers were about $7 \cdot 10^{17} \text{ cm}^{-3}$ using a conversion factor of $2.45 \cdot 10^{17} \text{ cm}^{-2}$ for the oxygen absorption band at 1108 cm^{-1} . The carbon and germanium concentrations were close to $1 \cdot 10^{17} \text{ cm}^{-3}$ and about $5 \cdot 10^{19} \text{ cm}^{-3}$ in the Cz-Si:C and Cz-Si:Ge, respectively. The wafer doped with germanium was carbon-lean, $N_{\text{CARBON}} < 5 \cdot 10^{16} \text{ cm}^{-3}$.

Square samples of $7 \times 7 \times 1 \text{ mm}^3$ were cut from these wafers. The electrical contacts were applied to samples in the Van der Pauw geometry. Samples were annealed at $T = 450^\circ\text{C}$ for $t = 10$ hours in pure argon under a hydrostatic pressure of $P = 1$ GPa. For comparison some reference samples were annealed under similar conditions at atmospheric pressure. After heat treatment a layer of about $50 \mu\text{m}$ were removed from sample surface by polishing and etching.

Hall effect measurements were taken with the aid of a computerized facility in the temperature range from $T = 20 \text{ K}$ to $T = 300 \text{ K}$.

3. Results

In Fig. 1 and Fig. 2 several $n(T)$ curves of the electron concentration *versus* reciprocal temperature are given for the initial and heat treated Cz-Si:Ge. It is known from the literature that the TDD formation in Cz-Si:Ge is retarded,⁴⁻⁶ despite the fact that in the presence of germanium the oxygen diffusivity increases.^{6,9} However, the TDDs are still a dominating family of thermal donors. Our data on the Cz-Si:Ge annealed at atmospheric pressure are in line with these findings. Actually, the initial formation rate of thermal donors in this material was found to be about $3 \cdot 10^{13} \text{ cm}^{-3} \cdot \text{h}^{-1}$. Without germanium the TDD formation rate in Cz-Si with similar oxygen contents is larger by a factor of two. The heat treatment of the same material for $t = 10$ hours under a pressure of $P = 1$ GPa resulted in a strong enhancement of the thermal donor

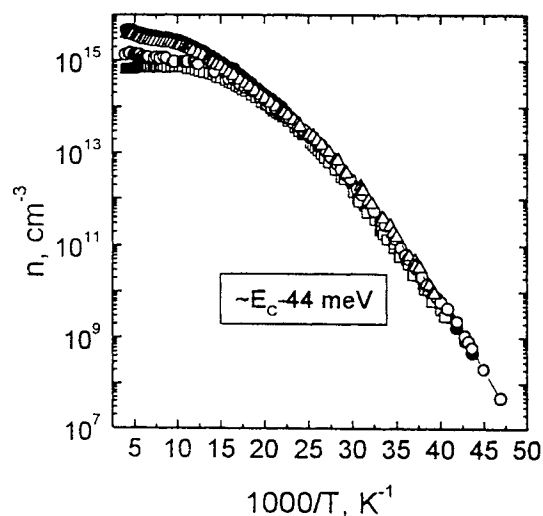


Fig. 1. Electron concentration vs reciprocal temperature in the Cz-Si:Ge heat treated at $T = 450^\circ\text{C}$ for $t = 10$ hours (open and black circles) and 120 hours (open triangles) under atmospheric pressure (open circles and triangles) and a hydrostatic pressure of $P = 1$ GPa (black circles). For comparison the $n(T)$ curve for the Cz-Si:Ge in the initial state is also shown (open squares). Activation energies of donor centers are given.

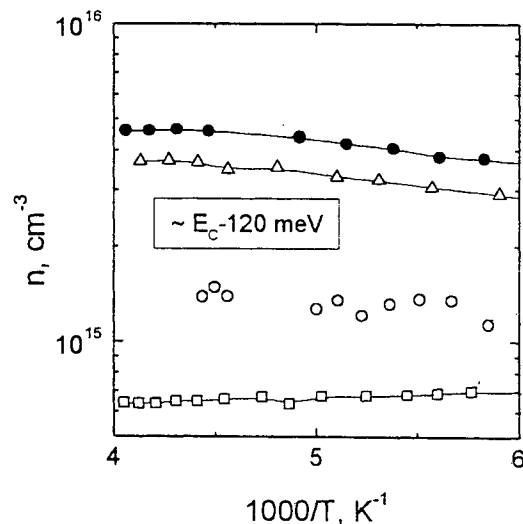


Fig. 2. Fragments of the $n(T)$ curves shown in Fig. 1.

formation (Fig. 2). As is seen, under such conditions of annealing the electron concentration at room temperature turned out to be larger than that after annealing of the same material for $t = 120$ hours at atmospheric pressure (Fig. 2). According to ⁵, the mechanism of TDD suppression in Cz-Si doped with germanium is mainly associated with decreasing capture radius of diffusing oxygen atoms by nucleation centers, precursors of forming TDDs. Both factors mentioned, increasing oxygen diffusivity and decreasing capture radius, are believed to be related to internal stress produced in Cz-Si:Ge by germanium atoms. In our case the high pressure applied to Cz-Si:Ge during heat treatment is thought to strongly enhance the oxygen diffusivity, thus changing the contributions of the factors considered. Optical measurements are now carried out to clarify this point.

Let us briefly discuss the role of carbon in heat-treated silicon. In Fig 3 and Fig. 4 several $n(T)$ curves are shown for the initial and annealed Cz-Si:C. A simple analysis of the $n(T)$ curves meets certain difficulties, since together with the TDDs other shallow donor centers also make their appearance during heat treatment at atmospheric pressure. This is not

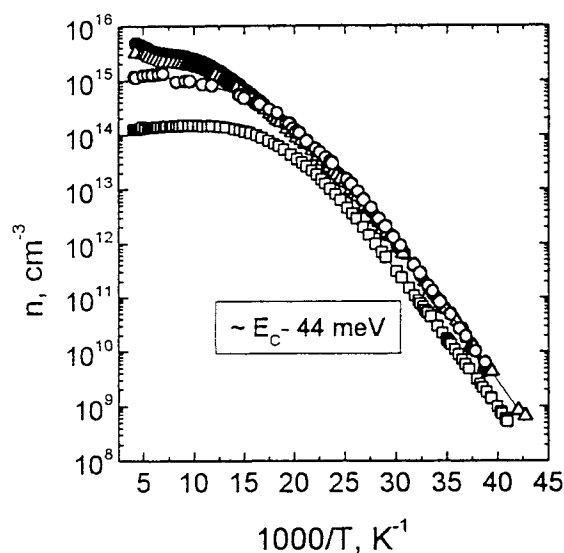


Fig. 3. Electron concentration vs reciprocal temperature in the Cz-Si:C heat treated at $T = 450^\circ\text{C}$ for $t = 10$ hours (open and black circles) and 60 hours (open triangles) under atmospheric pressure (open circles and triangles) and a hydrostatic pressure of $P = 1$ GPa (black circles). For comparison the $n(T)$ curve for the Cz-Si:Ge in the initial state is also shown (open squares). Activation energies of donor centers are given.

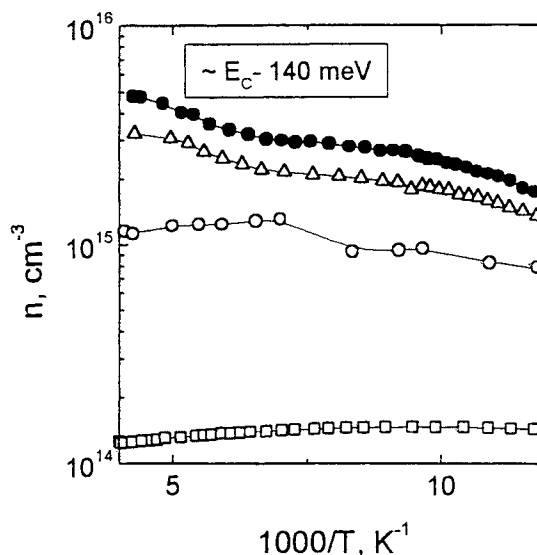


Fig. 4. Fragments of the $n(T)$ curves shown in Fig. 3.

surprising because of many quasichemical reactions of carbon with intrinsic defects and impurities, first of all oxygen.¹⁰ Besides, it is well known that as a result of oxygen agglomeration in Cz-Si self-interstitials are produced to relieve the strain around growing SiO_x precipitates.¹ Interactions of substitutional and interstitial carbon atoms with oxygen can be responsible for the appearance of additional centers in annealed Cz-Si:C. Suppression of the TDD formation in the presence of carbon is thought to be due to the overall strain relief in Cz-Si:C crystals associated with this dopant.¹ As a consequence, the driving force for oxygen agglomeration is weakened. The effect of hydrostatic pressure upon the formation processes of thermal donors in Cz-Si:C is similar to that observed in Cz-Si:Ge. In view of the different mechanisms of suppression of thermal donor formation in these materials one can conclude that their similar behavior under hydrostatic pressure is dictated by the same factor, mainly by increasing oxygen diffusivity under stress.

4. CONCLUSIONS

The formation processes of thermal donors in Cz-Si:C and Cz-Si:Ge annealed at $T = 450^\circ\text{C}$ under atmospheric and high pressure have been studied. Under normal conditions of heat treatment both isoelectronic impurities if present in large concentrations can retard markedly these processes. Heat treatment of Cz-Si:C and Cz-Si:Ge at $T = 450^\circ\text{C}$ under high pressure results in a strong enhancement of the thermal donor formation in both materials. The observed effect is thought to be due to increasing oxygen diffusivity under stress.

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